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(71) Applicant: **Central Glass Company, Limited**
Ube-shi, Yamaguchi 755-0001 (JP)

(72) Inventors:
- **Hayakawa, Naoya,**
Central Glass Company, Limited
Matsusaka-shi, Mie 515-0001 (JP)
- **Shimooka, Taishin,**
Central Glass Company, Limited
Matsusaka-shi, Mie 515-0001 (JP)

(74) Representative:
Manitz, Finsterwald & Partner GbR
Postfach 31 02 20
80102 München (DE)

(54) **Lead-free low-melting glass**

(57) The invention relates to a lead-free, low-melting glass for covering a substrate. This glass contains 0.1-25 wt% of SiO_2, 1-50 wt% of B_2O_3, 1-45 wt% of ZnO, 20-90 wt% of Bi_2O_3, 0.1-40 wt% of V_2O_5, 0-5 wt% of Nb_2O_5, 0-20 wt% of R_2O where R is Li, Na or K, and 0-20 wt% of RO where R is Mg, Ca, Sr or Ba. This glass has a thermal expansion coefficient of from 65×10^{-7}/°C to 100×10^{-7}/°C within a range of 30-300°C; and has a softening point of not higher than 630°C.

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Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a lead-free, low-melting glass for covering a substrate, particularly for covering a transparent electrode pattern or bus electrode pattern disposed on a plasma display panel (PDP) substrate. This glass serves as an electric insulating film of a PDP substrate.

[0002] It is general to use a transparent glass substrate as a substrate for electronic devices. Examples of such glass substrate are soda-lime-silica glasses and similar glasses (high strain-point glasses) and alumino-lime-borosilicate glasses that are low in alkali components or almost free therefrom. Their thermal expansion coefficients are from about $65 \times 10^{-7}/°C$ to about $100 \times 10^{-7}/°C$ within a range of 30-300°C. In case that a transparent glass substrate has thereon a film having a thermal expansion coefficient substantially different from that of the glass substrate, it may be possible to have defects such as exfoliation of the film and warping of the glass substrate. Furthermore, the above glass substrate has a high softening point of from about 720 to about 840°C. Thus, it is general to have a baking temperature exceeding 630°C, and thereby it may be possible to have a problem of deformation and thermal shrinkage of the substrate.

[0003] Hitherto, lead-containing glass has been used as a low-melting glass for covering a substrate. Lead is an important component for making the glass have a low melting point. However, there is a recent trend to avoid the use of lead due to its adverse effect on human and environment.

[0004] Japanese Patent Laid-open Publication JP-A-8-26770 discloses a sealing composition for plasma display panel, having a thermal expansion coefficient (of room temperature to 300°C) from $65 \times 10^{-7}/°C$ to $85 \times 10^{-7}/°C$.

[0005] JP-A-9-278483 discloses a bismuth-based glass composition comprising 20-80 wt% of Bi_2O_3, 5-35 wt% of B_2O_3, 0-35 wt% of BaO, and 0-30 wt% of SrO, wherein the total of BaO and SrO is from 5wt% to 40wt%.

[0006] JP-A-2000-128574 discloses a bismuth-based glass composition comprising 30-50 mol% of Bi_2O_3, 10-40 wt% of B_2O_3, and 1-10 wt% of the total of BaO and SrO. This glass composition has a thermal expansion coefficient that is higher than $100 \times 10^{-7}/°C$.

[0007] JP-A-2002-12445, corresponding to US Patent 6,475,605, discloses a SiO_2-B_2O_3-BaO-ZnO-based low-melting glass.

SUMMARY OF THE INVENTION

[0008] It is therefore an object of the present invention to provide a low-melting glass capable of easily providing a covering film that has a thermal expansion coefficient close to that of the substrate and a low softening point.

[0009] It is another object of the present invention to provide a low-melting glass, which is free from a problem of increasing resistance of transparent electrodes and bus electrodes formed on a PDP substrate, upon baking the low-melting glass formed on these electrodes.

[0010] According to a first aspect of the present invention, there is provided a lead-free, low-melting glass for covering a substrate. This glass (first glass) comprises 0.1-25 wt% of SiO_2, 1-50 wt% of B_2O_3, 1-45 wt% of ZnO, 20-90 wt% of Bi_2O_3, 0.1-40 wt% of V_2O_5, 0-5 wt% of Nb_2O_5, 0-20 wt% of R_2O where R is Li, Na or K, and 0-20 wt% of RO where R is Mg, Ca, Sr or Ba. The first glass has a thermal expansion coefficient of from $65 \times 10^{-7}/°C$ to $100 \times 10^{-7}/°C$ within a range of 30-300°C; and a softening point of not higher than 630°C.

[0011] According to a second aspect of the present invention, there is provided a lead-free, low-melting glass for covering a substrate. This glass (second glass) comprises 0.1-10 wt% of SiO_2, 5-25 wt% of B_2O_3, 1-35 wt% of ZnO, 40-90 wt% of Bi_2O_3, 0.1-5 wt% of V_2O_5, 0-5 wt% of Al_2O_3, 0-5 wt% of Nb_2O_5, 0-20 wt% of R_2O where R is Li, Na or K, and 0-20 wt% of RO where R is Mg, Ca, Sr or Ba. The second glass has a thermal expansion coefficient of from 65 $\times 10^{-7}/°C$ to $100 \times 10^{-7}/°C$ within a range of 30-300°C; and a softening point of not higher than 550°C.

[0012] According to a third aspect of the present invention, there is provided a lead-free, low-melting glass for covering a substrate. This glass (third glass) comprises 0.1-15 wt% of SiO_2, 10-50 wt% of B_2O_3, 5-50 wt% of ZnO, 0-20 wt% of R_2O where R is Li, Na or K, 0-5 wt% of Nb_2O_5, and 0.1-60 wt% of V_2O_5. The third glass has a thermal expansion coefficient of from $65 \times 10^{-7}/°C$ to $100 \times 10^{-7}/°C$ within a range of 30-300°C; and a softening point of not higher than 630°C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0013] Each of the above-mentioned first, second and third glasses is defined as being substantially free from PbO, with respect to the term "lead-free". In other words, these glasses may contain PbO in an amount of not greater than 0.3wt% as an impurity contained in a glass raw material and/or cullet. With this, it is possible to neglect adverse effects of PbO on human body, environment, insulation characteristics and the like. Hereinafter, each of the first, second and third glasses may be referred to as "the low-melting glass" for simplification.

[0014] The low-melting glass of the present invention is colorless and lead-free and has a suitable thermal expansion coefficient, a low softening point, and no reactivity with electrodes. Therefore, the low-melting glass is very useful for sealing, covering and rib formation in PDP, fluorescent display tube and the like.

[0015] The low-melting glass is used in the form of powder when it is used for sealing, covering and rib formation. According to need, the glass in the form of powder can be mixed with a low-expansion ceramic filler, a heat resistant pigment and the like, followed by kneading with an organic oil, thereby preparing a paste.

[0016] The substrate, which is to be covered by the low-melting glass, may be a transparent glass substrate, such as a soda-lime-silica glass or a similar glass (high strain point glass) or an alumino-lime-borosilicate glass. The substrate may have a thermal expansion coefficient of from about $65 \times 10^{-7}/°C$ to about $100 \times 10^{-7}/°C$ within a range of 30-300°C. The low-melting glass can have a thermal expansion coefficient close to that of the substrate. With this, it becomes possible to prevent exfoliation of the film from the substrate and/or warp of the substrate. The substrate may have a softening point of from about 720 to about 840°C. In contrast with this, the low-melting glass has a softening point of not higher than 630°C (in the case of the first and third glasses) or 550°C (in the case of the second glass). Therefore, when the film is baked, it become possible to prevent softening, deformation and thermal shrinkage of the substrate.

[0017] As mentioned above, it is possible to directly cover a substrate with the film of the low-melting glass, for example, in order to alter optical characteristics of the substrate. Furthermore, it is possible to form at least one of various functional films on the film of the low-melting glass. It is possible to prepare a frosted glass for reducing glare of the solar radiation and artificial illumination, by mixing a low-melting glass powder with a silica fine powder, an alumina fine powder and/or the like and by forming a film from the resulting mixture on a glass substrate.

[0018] The low-melting glass for covering a substrate is a glass that has a low softening point and softens at a temperature substantially lower than that of the glass substrate.

[0019] The first glass may be modified into a lead-free, low-melting glass (fourth glass) comprising 0.1-25 wt% of SiO_2, 1-40 wt% of B_2O_3, 1-45 wt% of ZnO, 20-90 wt% of Bi_2O_3, 0.1-5 wt% of V_2O_5, 0-5 wt% of Nb_2O_5, 0-20 wt% of R_2O where R is Li, Na or K, and 0-20 wt% of RO where R is Mg, Ca, Sr or Ba. The fourth glass also has a thermal expansion coefficient of from $65 \times 10^{-7}/°C$ to $100 \times 10^{-7}/°C$ within a range of 30-300°C; and a softening point of not higher than 630°C.

[0020] The description of chemical components of the low-melting glass is as follows. SiO_2 is a glass-forming component that is essential for making a stable glass. The SiO_2 content of the glass is preferably 0.1-25 wt%. If it is less than 0.1 wt%, the glass may become unstable to cause devitrification. If it is greater than 25 wt%, the softening point of the glass may become too high, making formability and workability difficult.

[0021] A PDP can be prepared by forming an insulating film to cover an electrode pattern and then by removing a portion of the insulating film with acid to expose a portion of the electrode pattern. If the SiO_2 content of the glass is excessive, the glass may become too high in acid resistance. Thus, it is preferably not greater than 25 wt% in order to smoothly decompose the film with acid. It is optional to replace half or less by weight of SiO_2 with Al_2O_3 to an extent that the Al_2O_3 content of the glass is not greater than 5 wt%. An Al_2O_3 content that is greater than 5wt% may cause devitrification. An Al_2O_3 content exceeding half of the SiO_2 content may make the glass too high in acid resistance. Therefore, it may become difficult to remove a portion of the insulating film.

[0022] Of the chemical components of the glass, B_2O_3 is a glass-forming component similar to SiO_2. B_2O_3 makes it easy to melt the glass, suppresses the excessive increase of the thermal expansion coefficient of the glass, and provides the glass with a suitable fluidity upon baking. The B_2O_3 content of the glass is 1-50 wt%, preferably 1-40 wt%. If it is less than 1 wt%, the glass may become unstable. Thus, devitrification tends to occur. If it exceeds 50 wt%, the softening point of the glass may become too high.

[0023] ZnO has functions of lowering the softening point of the glass, providing the glass with a suitable fluidity upon melting and adjusting the glass to having a suitable thermal expansion coefficient. The ZnO content of the glass is 1-45 wt%. If it is less than 1 wt%, these functions may become insufficient. If it is greater than 45 wt%, the glass may become unstable. Thus, devitrification tends to occur.

[0024] Similar to ZnO, Bi_2O_3 also has functions of lowering the softening point of the glass, providing the glass with a suitable fluidity upon melting and adjusting the glass to having a suitable thermal expansion coefficient. The Bi_2O_3 content of the glass is 20-90 wt%. If it is less than 20 wt%, these functions may become insufficient. If it is greater than 90 wt%, the thermal expansion coefficient may become too high.

[0025] V_2O_5 is a component for suppressing coloring of the glass. The V_2O_5 content of the glass is 0.1-40 wt%, preferably 0.1-5 wt%. If it is less than 0.1wt%, the coloring suppression may become insufficient. If it is greater than 40wt%, the glass may be made to have a black color.

[0026] The second glass is made possible by its chemical composition to have a thermal expansion coefficient of from $65 \times 10^{-7}/°C$ to $100 \times 10^{-7}/°C$ within a range of 30-300°C and a softening point of not higher than 550°C. Thus, the second glass can serve as a low-melting point (having an extremely low softening point) for film formation, rib formation and sealing on a transparent electrode pattern of a display panel substrate such as PDP.

[0027] In case that the film of the low-melting glass covers a transparent electrode pattern that is made of a first

oxide (e.g., at least one of In_2O_3, SnO_2 and In_2O_3 doped with Sn (ITO)) and disposed on a substrate of a display panel (e.g., PDP), it is preferable that the low-melting glass also contains 0.1-5 wt% of this first oxide so long as the first oxide does not interfere with the glass to have the above-mentioned thermal expansion coefficient and softening point. Similarly, in case that the film covers a bus electrode pattern that is made of a metal (e.g., at least one of Cu and Ag) and disposed on a substrate of a display panel (e.g., PDP), it is preferable that the low-melting glass also contains 0.1-1.5 wt% of an oxide (e.g., at least one of CuO and Ag_2O) of this metal. This oxide is referred to as "second oxide".

[0028] Due to the above containment of at least one of the above first and second oxides, it is possible to suppress the increase of resistance of the transparent electrode and the bus electrode after the formation of a low-melting glass layer on a PDP panel glass having such electrodes. If the first oxide content is less than 0.1wt%, it may not be possible to sufficiently suppress the resistance increase. In contrast, if it is greater than 5wt%, the low-melting glass may have devitrification. If the second oxide content is less than 0.1wt%, the advantageous effect of adding the second oxide may not be sufficient. In contrast, if it is greater than 1.5wt%, the low-melting glass may have a color.

[0029] Furthermore, due to the above containment of at least one of the above first and second oxides, it becomes possible to effectively suppress both of (1) a first corrosion of the low-melting glass by the transparent electrode pattern and/or the bus electrode pattern and (2) a second corrosion of the transparent electrode pattern and/or the bus electrode pattern by the low-melting glass. In particular, if the low-melting glass contains 0.1-1.5 wt% of CuO, the low-melting glass is provided with an advantageous filter function that makes blue color of PDP clearer. In fact, PDP is generally inferior in blue color emission. Therefore, the containment of a suitable amount of CuO is particularly preferable. If the amount of at least one of the above first and second oxides is too much, the low-melting glass may have inferior thermal characteristics and an undesirable color.

[0030] In case of directly covering a substrate with a film of the low-melting glass, the glass may contain additives of Fe_2O_3, Cr_2O_3, CoO, CeO_2, Sb_2O_3 and the like for providing the glass with a certain color, ultraviolet absorption capability, infrared shielding capability and the like, so long as these additives do not interfere with the glass to have the above-mentioned thermal expansion coefficient, softening point and dielectric constant. The total of the above additives is preferably not greater than 1 wt%.

[0031] An exemplary process for producing a front substrate of a PDP will be described as follows. This front substrate is made of a clear soda-lime glass or another glass having a chemical composition, thermal characteristics and the like similar to those of clear soda-lime glass. A transparent electrode pattern, for example, made of an ITO-based or SnO_2-based material is formed on a surface of the front substrate by sputtering or chemical vapor deposition (CVD).

[0032] Furthermore, a part of the transparent electrode pattern is covered with a bus electrode of Cr-Cu-Cr (Cu may be replaced with Ag or Al). Then, a transparent insulating film made of a low-melting glass according to the invention is formed on the surface of the front substrate in a manner to cover the front substrate, the transparent electrode pattern and the bus electrode pattern. In fact, this insulating film is prepared by mixing a low-melting glass powder, which has been adjusted to having a certain desired particle size, with a paste oil, then by applying the resulting mixture onto the front substrate and the transparent electrode pattern by screen printing or the like, and then by baking the resulting precursory film at about 630°C into an insulating film having a thickness of about 30 μm. This thickness of about 30 μm is considered to be a sufficient thickness to achieve display capability and display stability for a long time by gas discharge. Furthermore, a protective magnesia layer is formed on the insulating film by sputtering or the like, thereby completing the production of a PDP front substrate.

[0033] In some cases, there is a necessity to remove a portion of the insulating film by applying an acid for exposing and connecting a portion of the electrode with an outside lead wire. In these cases, the insulating film preferably has a suitable acid solubility.

EXAMPLES 1-10 & COMPARATIVE EXAMPLES 1-10

[0034] In each of these examples, a paste of a low-melting glass powder was prepared as follows. At first, raw materials of a low-melting glass powder were mixed together. The resulting mixture was put into a platinum crucible and then heated in an electric furnace at a temperature of 1,000-1,100°C for 1-2 hr, thereby obtaining a glass composition shown in Tables 1-4. In fact, a fine silica sand powder, boric acid, aluminum oxide, zinc white, barium carbonate, magnesium carbonate, calcium carbonate, strontium carbonate, bismuth oxide, lithium carbonate, sodium carbonate, potassium carbonate, red lead, ortho phosphate, indium oxide, tin oxide, copper oxide, and silver nitrate were respectively used as raw materials of SiO_2, B_2O_3, Al_2O_3, ZnO, BaO, MgO, CaO, SrO, Bi_2O_3, Li_2O, Na_2O, K_2O, PbO, P_2O_5, In_2O_3, SnO, CuO, and Ag_2O of the glass composition. A portion of the obtained glass composition was poured into a mold, and then the resulting glass block was used for the measurement of its thermal characteristics (thermal expansion coefficient and softening point). The rest of the obtained glass composition was formed into flakes by a rapid-cooling, dual-roller, forming machine, and then formed by a crushing machine into a glass powder having an average particle size of 2-4 μm and a maximum particle size of less than 15 μm. The obtained glass powder and a binder (ethyl cellulose) were mixed with a paste oil composed of α-terpineol and butyl carbitolacetate into a paste having a viscosity of about

300±50 poises, which is suitable for screen printing.

[0035] Separately, an ITO pattern film was formed by sputtering on a soda-lime glass substrate having a thickness of 2-3 mm and widths of 150 mm. Then, the above-obtained paste was applied to the glass substrate and the ITO pattern film by screen printing using a screen having a mesh opening of #250 in a manner to adjust an insulating film obtained by the following baking to having a thickness of about 30 μm. The resulting precursory film of the paste was baked at a temperature not higher than 630°C for 60 min, thereby forming an insulating film having a thickness of about 30μm.

[0036] The glass block of the low-melting glass was subjected to a measurement of thermal expansion coefficient, as follows. At first, the glass block was cut and ground into a test sample. This test sample was set on a thermal expansion tester. Then, the temperature of the test sample was increased at a rate of 5°C per minute in order to measure elongation of the test sample. Based on this, the average thermal expansion coefficient of the test sample within a range of 30-300°C was determined in terms of $\alpha \times 10^{-7}$/°C. The results are shown in Tables 1-4. For example, the result of Example 1 was 65×10^{-7}/°C, as shown in Table 1. It is preferable that the low-melting glass has a thermal expansion coefficient close to that of its substrate in contact with the low-melting glass. Thus, the thermal expansion coefficient of the low-melting glass is preferably from 65×10^{-7}/°C to 100×10^{-7}/°C.

[0037] The glass block of the low-melting glass was formed by heating into a glass beam having a predetermined size. This glass beam was set on a Lyttelton viscometer. Then, the temperature of the glass beam was increased, and its softening point, that is, a temperature at which viscosity coefficient (η) reached $10^{7.6}$ was measured. The results are shown in Tables 1-4.

[0038] The coated glass substrate having the glass substrate (thickness: 3mm; visible light transmittance: 86%) coated with the ITO film and the insulating film was subjected to a transmittance measurement with a spectrophotometer to determine the average transmittance in the visible region. The results are shown in Tables 1-4. It is preferable that the coated glass substrate has a visible light transmittance of 70% or greater.

[0039] After the removal of the insulating film from the coated glass substrate, the electric resistance of the ITO film was measured by a four probe method. This ITO film resistance divided by the ITO film resistance measured prior to the insulating film formation thereon was determined as "ITO resistance increase rate". The results are shown in Tables 1-4. It should be noted that the ITO film resistance increases, if the insulating film is formed on the ITO film, due to the mutual corrosion of the ITO film and the insulating film. The ITO resistance increase rate is preferably not greater than 250%.

[0040] Separately, an ITO pattern film was formed on a glass substrate having widths of 30 mm. Then, a bus electrode was formed on the glass substrate to cover a part of the ITO pattern film. After that, the above-obtained paste was applied and then baked, thereby forming an insulating film. The resulting sample was observed with a microscope. In this observation, it was judged as "good" when no bubbles (size: 30 μm or greater) were found around the bus electrode, and as "failure" when such bubbles were found therearound.

[0041] In Comparative Examples 4 and 10, vitrification did not occur.

Table 1

	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5
Glass Composition (%)					
SiO_2	21.5	3.5	6.2	1.0	19.6
B_2O_3	3.0	36.9	24.5	6.6	5.0
ZnO	32.5	35.1	43.1	3.4	34.7
Bi_2O_3	42.0	22.5	24.5	86.1	40.3
V_2O_5	0.2	0.5	1.5	0.2	0.1
Al_2O_3	0.3	--	--	0.5	--
SnO	0.1	--	--	--	0.1
In_2O_3	0.2	1.5	0.1	2.0	--
CuO	0.2	0.5	0.1	--	0.2
Ag_2O	--	--	--	0.2	--
Thermal Expansion Coefficient (α)	65	79	72	100	66
Softening Point (°C)	625	550	591	411	610

Table 1 (continued)

	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5
Glass Composition (%)					
Visible Light Transmittance (%)	71	75	73	80	72
ITO Resistance Increase Rate (%)	200	210	200	250	200
Coloring of Red Brown Color	No	No	No	No	No
Stability	Good	Good	Good	Good	Good

Table 2

	Com. Ex.1	Com. Ex.2	Com. Ex.3	Com. Ex.4	Com. Ex.5
Glass Composition (%)					
SiO_2	26.0	--	0.9	13.0	0.7
B_2O_3	10.0	43.0	4.2	15.0	0.8
ZnO	61.0	51.0	3.6	53.0	--
Bi_2O_3	3.0	6.0	91.3	18.0	92.5
V_2O_5	--	--	--	--	--
In_2O_3	--	--	--	--	5.5
CuO	--	--	--	2.0	--
Ag_2O	--	--	--	--	--
SnO	--	--	--	--	0.5
Thermal Expansion Coefficient (α)	43	--	102	51	--
Softening Point (°C)	672	--	438	640	--
Visible Light Transmittance (%)	61	--	72	53	--
ITO Resistance Increase Rate (%)	260	--	440	280	--
Reaction with Bus Electrode	Good	--	Failure	Good	--
Coloring of Red Brown Color	Yes	--	Yes	Yes	--
Stability	Good	--	Failure	Good	--

Table 3

	Ex.6	Ex.7	Ex.8	Ex.9	Ex.10
Glass Composition (%)					
SiO_2	2.5	9.3	3.1	3.2	0.7
B_2O_3	24.3	10.5	14.2	12.2	6.2
ZnO	32.0	26.7	14.2	10.2	3.0
Bi_2O_3	40.8	52.7	67.4	72.0	86.0
V_2O_5	0.1	0.2	0.5	0.5	1.1
Al_2O_3	0.0	--	--	0.2	0.5
SnO	0.1	--	--	--	--
In_2O_3	0.1	0.5	0.5	1.5	2.0
CuO	0.1	0.1	0.1	--	0.5

Table 3 (continued)

	Ex.6	Ex.7	Ex.8	Ex.9	Ex.10
Glass Composition (%)					
Ag_2O	--	--	--	0.2	--
Thermal Expansion Coefficient (α)	65	70	79	90	100
Softening Point (°C)	550	542	501	456	411
Visible Light Transmittance (%)	71	72	76	79	80
ITO Resistance Increase Rate (%)	180	180	200	220	250
Coloring of Red Brown Color	No	No	No	No	No
Stability	Good	Good	Good	Good	Good

Table 4

	Com. Ex.6	Com. Ex.7	Com. Ex.8	Com. Ex.9	Com. Ex.10
Glass Composition (%)					
SiO_2	6.1	11.0	8.0	2.0	0.5
B_2O_3	23.6	15.1	12.2	29.5	1.0
ZnO	32.1	32.3	38.7	16.3	--
Bi_2O_3	38.2	41.6	41.1	52.2	92.5
V_2O_5	--	--	--	--	--
In_2O_3	--	--	--	--	5.5
CuO	--	--	--	--	--
Ag_2O	--	--	--	--	--
SnO	--	--	--	--	0.5
Thermal Expansion Coefficient (α)	60	59	59	65	--
Softening Point (°C)	557	567	556	555	--
Visible Light Transmittance (%)	70	65	71	72	--
ITO Resistance Increase Rate (%)	260	230	260	280	--
Reaction with Bus Electrode	Failure	Failure	Failure	Failure	--
Coloring of Red Brown Color	Yes	Yes	Yes	Yes	--
Stability	Good	Good	Failure	Good	--

[0042] The entire disclosure of Japanese Patent Application Nos. 2002-122770 filed on April 24, 2002 and 2003-18830 filed on January 28, 2003, including specification, claims and summary, is incorporated herein by reference in its entirety.

Claims

1. A lead-free, low-melting glass for covering a substrate, said glass comprising:

   0.1-25 wt% of SiO_2, 1-50 wt% of B_2O_3, 1-45 wt% of ZnO, 20-90 wt% of Bi_2O_3, 0.1-40 wt% of V_2O_5, 0-5 wt% of Nb_2O_5, 0-20 wt% of R_2O where R is Li, Na or K, and 0-20 wt% of RO where R is Mg, Ca, Sr or Ba; and having a thermal expansion coefficient of from 65×10^{-7}/°C to 100×10^{-7}/°C within a range of 30-300°C; and having a softening point of not higher than 630°C.

2. A glass according to claim 1, wherein said glass comprises 1-40 wt% of said B_2O_3 and 0.1-5 wt% of said V_2O_5.

3. A lead-free, low-melting glass for covering a substrate, said glass comprising:

   0.1-10 wt% of SiO_2, 5-25 wt% of B_2O_3, 1-35 wt% of ZnO, 40-90 wt% of Bi_2O_3, 0.1-5 wt% of V_2O_5, 0-5 wt% of Al_2O_3, 0-5 wt% of Nb_2O_5, 0-20 wt% of R_2O where R is Li, Na or K, and 0-20 wt% of RO where R is Mg, Ca, Sr or Ba; and
   having a thermal expansion coefficient of from 65×10^{-7}/°C to 100×10^{-7}/°C within a range of 30-300°C; and having a softening point of not higher than 550°C.

4. A lead-free, low-melting glass for covering a substrate, said glass comprising:

   0.1-15 wt% of SiO_2, 10-50 wt% of B_2O_3, 5-50 wt% of ZnO, 0-20 wt% of R_2O where R is Li, Na or K, 0-5 wt% of Nb_2O_5, and 0.1-60 wt% of V_2O_5; and
   having a thermal expansion coefficient of from 65×10^{-7}/°C to 100×10^{-7}/°C within a range of 30-300°C; and having a softening point of not higher than 630°C.

5. A glass according to one of claims 1-4, which directly covers the substrate or covers an element disposed on the substrate, said element comprising at least one of a conducting material and a semiconductor pattern.

6. A glass according to one of claims 1-4, which covers an element disposed on the substrate that is used for a display panel, said element comprising at least one of a transparent electrode pattern and a bus electrode pattern.

7. A glass according to claim 6, wherein, when said element comprises said transparent electrode pattern made of an oxide, said glass also comprises 0.1-5 wt% of said oxide.

8. A glass according to claim 7, wherein said oxide is at least one selected from the group consisting of In_2O_3, SnO_2, and In_2O_3 doped with Sn (ITO).

9. A glass according to claim 6, wherein, when said element comprises said bus electrode pattern made of a metal, said glass also comprises 0.1-1.5 wt% of an oxide of said metal.

10. A glass according to claim 9, wherein said oxide is at least one selected from the group consisting of CuO and Ag_2O.

11. A glass according to claim 6, wherein, when said element comprises said transparent electrode pattern made of an oxide, and said bus electrode pattern made of a metal, said glass also comprises 0.1-5 wt% of said oxide and 0.1-1.5 wt% of an oxide of said metal.

12. A laminate comprising:

   (a) a substrate; and
   (b) a film covering said substrate, said film comprising a lead-free, low-melting glass according to one of claims 1-4.

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EUROPEAN SEARCH REPORT

Application Number
EP 03 00 9192

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	US 6 105 394 A (EMLEMDI HASAN B ET AL) 22 August 2000 (2000-08-22) * the whole document * ---	1-12	C03C3/066 C03C8/24
A	US 5 629 247 A (PRUNCHAK ROBERT) 13 May 1997 (1997-05-13) * the whole document * ---	1-12	
A	SU 1 252 310 A (KOSTOMAROV VLADIMIR S;KHARLAMOVA LIDIYA P; SMOLSKAYA SVETLANA S; PRISH) 23 August 1986 (1986-08-23) * the whole document * ---	1-12	
A	SU 1 169 951 A (ERMOLENKO NIKOLAJ N ;MANCHENKO ZINAIDA F (SU); KARPOVICH ELENA F () 30 July 1985 (1985-07-30) * the whole document * ---	1-12	
A	SU 1 477 706 A (BRUSS POLT I) 7 May 1989 (1989-05-07) * the whole document * ---	1-12	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	SU 947 102 A (BRUSS TI KIROVA) 30 July 1982 (1982-07-30) * the whole document * ---	1-12	C03C
A	SU 923 976 A (BRUSS TI KIROVA) 30 April 1982 (1982-04-30) * the whole document * ---	1-12	
A	SU 775 061 A (BRUSS POLT I) 30 October 1980 (1980-10-30) * the whole document * --- -/--	1-12	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	19 August 2003	Somann, K

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

Application Number
EP 03 00 9192

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 328 (C-0860), 21 August 1991 (1991-08-21) -& JP 03 126639 A (NIPPON ELECTRIC GLASS CO LTD), 29 May 1991 (1991-05-29) * abstract * ---	4-12	
X	US 5 051 381 A (OHJI MASAHIKO ET AL) 24 September 1991 (1991-09-24) * examples * ---	4-12	
X	SU 557 062 A (LENINGRAD LENSOVET TECH) 5 May 1977 (1977-05-05) * the whole document * ---	4-12	
X	SU 547 401 A (LENINGRAD LENSOVET TECH) 25 February 1977 (1977-02-25) * the whole document * ---	4-12	
X	PATENT ABSTRACTS OF JAPAN vol. 010, no. 128 (C-345), 13 May 1986 (1986-05-13) -& JP 60 255643 A (HITACHI SEISAKUSHO KK), 17 December 1985 (1985-12-17) * abstract * ---	4-12	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
X	FR 2 348 897 A (LABO ELECTRONIQUE PHYSIQUE) 18 November 1976 (1976-11-18) * the whole document * -----	4-12	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	19 August 2003	Somann, K

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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19-08-2003

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 6105394	A	22-08-2000	EP	1150926 A1	07-11-2001
			WO	0041977 A1	20-07-2000
US 5629247	A	13-05-1997	AU	3204197 A	26-11-1997
			WO	9742128 A1	13-11-1997
SU 1252310	A	23-08-1986	SU	1252310 A1	23-08-1986
SU 1169951	A	30-07-1985	SU	1169951 A1	30-07-1985
SU 1477706	A	07-05-1989	SU	1477706 A1	07-05-1989
SU 947102	A	30-07-1982	SU	947102 A1	30-07-1982
SU 923976	A	30-04-1982	SU	923976 A1	30-04-1982
SU 775061	A	30-10-1980	SU	775061 A1	30-10-1980
JP 03126639	A	29-05-1991	NONE		
US 5051381	A	24-09-1991	JP	2042046 C	09-04-1996
			JP	2289445 A	29-11-1990
			JP	7064588 B	12-07-1995
SU 557062	A	05-05-1977	SU	557062 A1	05-05-1977
SU 547401	A	25-02-1977	SU	547401 A1	25-02-1977
JP 60255643	A	17-12-1985	NONE		
FR 2348897	A	18-11-1977	FR	2348897 A1	18-11-1977

EPO FORM P0459

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